The Electrical Resistance and the Critical Point of Mercury

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Values are given for the relative resistance, the instantaneous pressure coefficient of resistance and the instantaneous temperature coefficient of resistance of liquid mercury in the region between 0° and 1200°C, and 1 and 4000 atmospheres. All of these quantities increase with rising temperature and decrease with rising pressure in this region. With the assumption that the resistance must be a continuous function of the temperature, for pressures higher than the critical pressure, the critical constants of mercury have been determined as 1460 ± 20°C and 1640 ± 50 kg/cm².

INTRODUCTION

THE resistivities at atmospheric pressure of a large number of liquid metals have been measured by various writers, including de la Rive,[1] Vincentini and Omodei,[2] Northrup,[3] Tsutsumi,[4] and Matsuyama.[5] The resistance of eight liquid metals, including the alkali metals, has been measured by Bridgman[6] at high pressures up to 100°C. It appeared of interest to observe the conductivity of a liquid metal over a larger proportion of its region of existence, combining high temperatures with high pressures. The metal chosen was mercury for the obvious reasons of accessibility of the liquid phase and unusual chemical purity. Still another reason was this: not only are the melting and boiling points of mercury at atmospheric pressure readily attainable, but there was cause to believe that its liquid—vapor critical point would also be within reach.

From general considerations, one would expect that above the critical pressure increase of temperature at constant pressure would be accompanied by a continuous change of resistivity; below the critical pressure, the phenomenon of boiling is possible with a discontinuous change of resistivity. This seems so certain that it may be accepted as a criterion for detecting the critical point, and its application leads to the values 1460°C and 1640 kg/cm² for the critical temperature and pressure.

DESCRIPTION OF APPARATUS

The pressure apparatus consisted of three steel cylinders and a pump; two of the cylinders contained moving pistons and were used to produce the desired pressure in the third or test cylinder. Details of the pressure tech-

[1] De la Rive, Arch. des Sci. Phys. (Geneva) **17**, 362 (1863).
[2] Vincentini and Omodei, Atti. Acc. Soc. Torino **25**, 90 (1889).
[3] Northrup, Jour. Frank. Inst. **177**, 1,287 (1914); **178**, 85 (1917).
[4] Tsutsumi, Sci. Rep (Tohoku) **7**, 93 (1918).
[5] Matsuyama, Sci. Rep. (Tohoku) **16**, 447 (1927).
[6] Bridgman, Proc. Am. Acad. **56**, 61 (1921).

nique may be found in the papers of P. W. Bridgman.[7] The pressure fluid in the test cylinder and the connecting system was nitrogen, the pump and its system using a mixture of glycerine and water. In the test cylinder was placed a small furnace made of concentric tubes of fused quartz, with helical windings of molybdenum wire. The mercury to be studied was placed in the innermost tube; next came a thermocouple, then a quartz tube for insulation, then the first heating coil, another quartz tube and finally another furnace winding. These tubes were all open at one end so that the pressure acted on both sides of the quartz walls. This furnace was assembled in a thin-walled steel tube, the spaces filled with zirconium oxide to act as a thermal insulator and to reduce convection in the nitrogen, and placed in the test cylinder. Electrical connections were made through a plug with six insulated conductors, the plug being held down by a large screw at the top of the cylinder.

The resistance of the mercury was measured in two ways, with a Carey-Foster bridge, and with a null-substitution potentiometer method. The results with these two methods, which involve different corrections, were in good agreement. When the bridge is employed, the resistance of the entire circuit is measured, including that of the mercury at the desired temperature, of some mercury at lower temperatures, of the leads, contacts and so on. In order to reduce the extraneous resistance to as small a fraction as possible, the mercury container was drawn down to a fine constriction for about 1 cm near its center; this constricted portion was placed in the hottest part of the furnace, and its resistance when filled with mercury at room temperature, was about ten times that of the rest of the circuit. As the temperature of the furnace increased, the resistance of the rest of the circuit increased, but not so fast as that of the constricted portion. Special runs gave a sufficiently accurate knowledge of this increase of lead resistance with furnace temperature to permit a correction, with a final uncertainty from this cause not exceeding one percent.

The use of the potentiometer demanded the construction of a four-terminal conductor. This was accomplished by passing fine quartz tubes inside the mercury container from the two ends, up to the constricted portion. The threads of mercury inside these fine tubes were thus insulated from the mercury cylinders between the fine tubes and the walls of the mercury container. The former served as potential leads, the latter as current leads. The resistance of the leads being eliminated by this method, the constricted portion of the container could be very short, with correspondingly decreased temperature difference over the important region.

Contact with the mercury must of course be made somewhere with solid wires, so that thermal electromotive forces are introduced if the contacts are at different temperatures. The contacts were therefore removed as far as possible from the furnace, by the use of mercury containers about 18 cm long with the contacts near the ends. The remaining thermal e.m.f. was eliminated when using the bridge by keeping the galvanometer circuit permanently closed and reading from a false zero on application of the bridge current.

[7] See for example, P. W. Bridgman, *The Physics of High Pressure*, Macmillan.

When using the potentiometer, it was necessary to take readings with the current reversed, adopting the mean value.

The furnace generally consisted of two concentric windings of 0.010 inch molybdenum wire, the inner one of about 5 feet of wire wound closely on a tube of one-quarter inch diameter, so that the length of the winding was 1.5 inches, the outer one wound on a tube fitting closely over the inner, of about 12 feet of wire forming a coil 2.5 or 3 inches long. With these two windings connected in parallel, a current of 5 amperes was sufficient to give temperatures of the order of 1200°C. This temperature existed in a small region which included the junction of the thermocouple and the constricted portion of the mercury container if this was made sufficiently short.

The chief difficulty in using a thermocouple in the interior of a high pressure cylinder is to bring the fine wires of the thermocouple to the exterior through the pressure packing, especially in the case of couples of platinum and its alloys. If this can be done, the cold junctions may be kept at 0°C and the only uncertainties are those arising (1) from the effect of pressure on the thermal e.m.f. and (2) from the effect of stress gradients combined with temperature gradients in those parts of the wires in the packing. The uncertainty from the first of the causes should not exceed 8° at 1200°C and 4000 atm.[8] for the couple employed, of platinum and platinum-10 percent rhodium. The second effect cannot be estimated but is certainly quite small.

Electrical connections between the inside and outside of the test cylinder were made by means of suitably insulated and packed steel conductors, situated in the plug at the top of the cylinder. A special device was employed for the thermocouple leads. Two of the steel conductors, which were about 3 inches long, were drilled with a 0.030 inch drill to within one-quarter inch of the ends which extended inside the cylinder; the holes were completed with a 0.013 inch drill. Wires of platinum and of platinum-10 percent rhodium, 0.010 inch in diameter, were passed one through each of these conductors and soldered at the inner ends, in the fine holes; for the rest of the length they were insulated from the steel by thin glass tubes. When the thermocouple on the inside was soldered to these leads the thermoelectric circuit was perturbed only by the contact over a small region of each wire with a mass of steel and solder, itself completely insulated from everything else. So long as the temperature was uniform over these contacts, no additional e.m.f. was introduced, and the steel pieces were sufficiently large, and far enough removed from the furnace so that this condition was very closely satisfied.

The electromotive force of the couple was measured with a Leeds and Northrup potentiometer and a Pye galvanometer, the combination being sensitive to 1 microvolt, corresponding with this couple to one-tenth degree. The pressure in the test cylinder was given by the change of resistance of a man-

[8] P. W. Bridgman, Proc. Am. Acad. **53**, 346 (1918). These measurements extend only to 100°C, for platinum alone; the temperature coefficient of thermal e.m.f. seems to decrease, however, as the temperature rises. The assumptions are made that it remains constant up to 1200°, and that the coefficient of platinum-rhodium has the same sign.

ganin gauge coil, placed in a separate steel block connected by a pipe which passed through the water bath surrounding the test cylinder. The temperature of the gauge coil was independent of the temperature of the furnace; and the pressures may be considered exact to within 10 kg/cm².

Electrical Resistance

Tables I, II and III contain the smoothed results of a large number of independent runs, using different mercury containers, different methods of

Table I. *Relative resistance of liquid mercury.*

t°C	$p=0$	500	1000	2000	3000	4000 kg/cm³
0	1.00	0.985	0.97	0.94	0.91	0.89
100	1.10	1.08	1.06	1.02	0.99	0.97
200	1.21	1.18	1.16	1.12	1.08	1.04
300	1.35	1.32	1.28	1.23	1.18	1.13
400		1.46	1.42	1.36	1.30	1.24
500		1.65	1.59	1.51	1.43	1.36
600		1.89	1.80	1.69	1.60	1.51
700		2.19	2.06	1.91	1.79	1.67
800		2.61	2.40	2.18	2.02	1.86
900		3.11	2.83	2.51	2.30	2.11
1000		3.90	3.48	2.96	2.68	2.43
1100		4.95	4.38	3.56	3.11	2.82
1200				4.53	3.77	3.31
1300					4.65	4.04

Table II. *Instantaneous pressure coefficient of resistance.* $(1/\omega)(\partial\omega/\partial p)_T \cdot 10^5$.

t°C	$p=0$	500	1000	2000	3000	4000 kg/cm²
0	3	3	3	3	3	3
100	4	4	3	3	3	3
200	4	4	4	4	4	4
300		5	5	4	4	4
400		6	6	4	4	4
500		7	7	5	5	5
600		10	9	6	6	6
700		14	11	7	7	7
800		17	14	8	8	7
900		21	17	10	9	8
1000		26	20	12	10	9
1100		33	24	17	13	10
1200				24	15	11
1300					18	12

Table III. *Instantaneous temperature coefficient of resistance.* $(1/\omega)(\partial\omega/\partial T)_p \cdot 10^4$.

t°C	$p=0$	1000	2000	3000	4000 kg/cm²
0	9.5	9.0	8.5	7.5	7.5
100	10.5	10	9	8	7.5
200	13.5	12	10	9	8
300	14.5	13	12	10	9
400		15	13	12	11
500		18	16	15	13
600		24	19	17	15
700		30	23	20	17
800		38	28	24	21
900		53	37	31	26
1000		82	56	45	39

measuring the resistance and different furnaces and thermocouples. The runs were all made at approximately constant pressure, varying the temperature from room temperature to the maximum desired and retracing the curve on cooling. The values of resistance are all relative to the value for 1 atmosphere (zero gauge pressure) and 0°C. The change of dimensions of the quartz mercury container is neglected; such data as are available indicate that the correction due to thermal expansion and compressibility of the quartz would not exceed one-third of 1 percent at 4000 atmospheres, which is less than the other uncertainties. At 1100°C, the various runs agree to within 3 percent; at lower temperatures, the uncertainty is smaller, probably not exceeding one-half percent below 500°C.

Critical Point

A rather extensive literature has grown up concerning the critical constants of mercury, including experimental and theoretical attacks upon the problem. A bibliography which I hope is complete is given below.[9–24] Estimates of the critical constants by comparison of the vapor-pressure curve of mercury with that of argon were given by Happel[12] as 1100°C and 456 atm., by Ariés[18] as 1080°C and 420 atm.; using another method, van Laar[19] obtained 900°C and 179 atm. Observations up to 1430°C failed, however, to disclose the critical point. Bernhardt[24] traced the boiling curve of mercury to 1435°C and 2000 atm., concluding that the critical point lay at a still higher temperature and pressure. Since my measurements lead me to conclude that the critical constants are about 1460°C and 1640 atm., a brief comparison of my method with that of Bernhardt seems desirable.

The apparatus which I used for detecting the critical point was essentially the same as that already described for measuring the resistance, except that the mercury container was made still smaller, permitting a more efficient furnace assembly, and the external circuit connected in series with the mercury column consisted simply of a milliammeter, a resistance of about 150 ohms and a dry cell. As the temperature approaches the critical temperature, the rate of increase of electrical resistance with temperature becomes so rapid

[9] Cailletet, Colardeau et Rivière, C. R. **130,** 1585 (1900).
[10] Strutt, Phil. Mag. **4,** 596 (1904).
[11] Traube and Teichner, Ann. d. Physik **13,** 620 (1904).
[12] Happel, Ann. d. Physik **13,** 351 (1904).
[13] Koenigsberger, Chem. Ztg. **36,** 1321 (1912).
[14] Menzies and Smith, Amer. Chem. Soc. **32,** 1432 (1910).
[15] Menzies, Amer. Chem. Soc. **35,** 1085 (1913); **41,** 1783 (1919).
[16] Thorpe and Rucker, Journ. Chem. Soc. **35,** 1065 (1913).
[17] Bender, Phys. Zeits. **16,** 246 (1915); **19,** 410 (1918).
[18] Ariés, C. R. **166,** 334 (1918).
[19] Van Laar, Versl. K. Ak. van Wetensch. **25,** 1498 (1917).
[20] Rassow, Zeits. f. anorg. Chem. **114,** 117 (1920).
[21] Walden Zeits. f. anorg. Chem. **112,** 1087 (1920).
[22] Weber, Comm. Phys. Lab. Leiden, Supp. 43 to Nos. 145–156, p. 23 (1920).
[23] Meyer, Phys. Zeits. **22,** 76 (1921).
[24] Bernhardt, Phys. Zeits. **26,** 265 (1925).

that the use of a bridge for measuring the resistance is not practicable unless the temperature can be maintained constant to within a small fraction of a degree. This was not possible under the conditions of this experiment, so the following procedure was adopted. The pressure being approximately constant, and having any desired value, the mercury was heated slowly and the current through the milliammeter was observed. At low temperatures, this current was about 10 milliamperes, for the resistance of the mercury cold was a few hundredths of an ohm (there was no constriction in the mercury containers used for this purpose). If the pressure was low enough to permit boiling, then at a well-defined temperature, the current fell brusquely to the zero of the instrument, indicating a relative resistance of the vapor of not less than 10^6. In this way the boiling curve was traced, up to a certain pressure above which the character of the phenomenon became quite different. At 1640 atm., and at higher pressures, the fall of the current was no longer abrupt; as the temperature increased the current decreased, first slowly, then rapidly, but permitting readings of current and temperature to be taken up to temperatures well beyond the prolongation of the boiling curve, where the current was not yet zero, nor in fact less than abuot 1/10 m.a.

It may be objected that the small residual current at these high temperatures was due to conduction by the quartz container. I think that the resistivity of the quartz is not of the right order of magnitude. If we suppose it to be about 10^5 ohms/cm^3 at 1500°C, which does not seem too high, then the current from a 1.5 volt cell through a section 5 mm long of a tube with a 1 mm bore and 2 mm outside diameter, will be about 10^{-6} amperes. But the smallest current observed was about 10^{-4} amperes, so that conduction by the quartz does not explain even the residual current at the highest temperatures, and *a fortiori*, does not account for the larger currents observed at slightly lower temperatures. Furthermore, conduction by the quartz would not be expected to vary greatly with a change of pressure from 1500 to 1700 atm., whereas the nature of the phenomenon changes completely in this region.

Additional weight to the interpretation of this behavior as indicating the critical region is provided by comparison of the current-temperature curves at different pressures above 1600 atm. It would be expected, I think, that these curves would move toward higher temperatures and tend to flatten out as the pressure increased. This is in fact the case, at 2040 atm. the drop from 10 to 0.1 milliampere is spread over about 70°, whereas at 1750 atm. it takes place in about 40° and at 1640 atm. in 15°. At 2040 atm., the resistivity still increases about 100 times between 1520° and 1540°.

The last remark leads to an explanation of the effect observed by Bernhardt, who heated a thin cylinder of mercury by passing a low-voltage alternating current through the mercury itself, detecting boiling up to 2020 atm. by oscillations of the heating current and constancy of the temperature. But oscillations would also be observed under these circumstances if the resistance increased notably in any small temperature range, and this is what I have observed in the region above 1600 atm. The heating of the mercury in my

apparatus was independent of the resistance of the mercury, so that it was possible to reach temperatures which could not be obtained, without arcing or using a high-voltage source, by passing a current through the mercury itself. Bernhardt's temperatures for the boiling curve are also slightly different from mine, being generally lower by about 20–30°. A variety of causes may be responsible for this, in particular the fact that Bernhardt's thermocouple made connections with steel conductors on the inside of the pressure cylinder. The temperature of the junctions could only be estimated and the error on these estimates enters directly in the final temperature.

It is difficult to give the resistivity corresponding to any given current through the mercury, because the length of the mercury column at the maximum temperature is not known. Using a mercury container with a very short constricted section, and a potentiometer, a few fairly precise values were obtained for the higher pressures, which could be used to obtain approximate values in the critical region. These are tabulated in Table IV, along with some measurements of Northrup[25] on the resistance of the vapor at 1 atm. The resistances are given relative to the resistance of the liquid at 0°C and 1 atm.

TABLE IV. *Relative resistance of mercury, times 10^{-6}.*

t°C	1 atm.	1640	1750	1870	2700
900	250				
1000	125				
1100	75	——— In this region, see Table I. ———			
1200	35				
1300	19				
1400	7			0.00002	0.000009
1500	3	0.12	0.08	0.0006	0.000017
1600				0.06	

It will be remarked that whereas the resistance of the vapor at 1 atm. decreases with rising temperature, the resistance at pressures well above the critical pressure increases with rising temperature, as does that of the liquid. Somewhere in between must be a region of resistance independent of the temperature.

CONCLUDING REMARKS

The variation of resistance of liquid mercury with pressure and temperature does not follow any simple law, nor is the resistivity simply related to the specific volume, so far as can be judged from the volume data available. Above 100°C, the specific volume is known only along the boiling curve, from the work of Bender.[17] Along this curve, the resistivity of the liquid increases much faster than does its volume.

The critical constants, as determined by the continuous variation of resistance with temperature at constant pressure, are 1460 ± 20°C and 1640 ± 50 kg/cm^2. These values are consistent with the data of Bender for the density of mercury and with the critical temperature deduced by Meyer[23]

[25] Northrup, Jour. Frank. Inst. July, 85 (1914).

from the temperature variation of surface tension. In conjunction with the data of Bender, the critical density is found to be about 5.[22] The critical pressure is much higher than any predicted by comparison with ordinary gases, leading to a value of the ratio RT_c/p_cv_c equal to 2.18. This is lower than the corresponding ratio for any substance hitherto studied, van der Waals' equation giving 2.66, while for hydrogen it is 2.86 and for most substances greater than 3.